Gas-condensate migration and oil fractionation in deltaic systems*

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The term *evaporative fractionation* is proposed to describe several phenomena involved in the secondary alteration of reservoired oil. Firstly, it is suggested that oil is frequently partially vaporized in the reservoir; secondly, that gas, bearing substantial portions of the oil in solution, is conducted along faults to form independent gas-condensate accumulations; thirdly, that residual oils formed in this fashion bear internal evidence of fractionation. In addition to the conspicuous loss of light ends, there is an increase in the content of light aromatic and naphthenic hydrocarbons relative to paraffins in the residual oil. Evaporative fractionation effects are recognized for the first time in the distillation and physical property data of US Bureau of Mines Routine Method Oil Analyses. Fractionation effects are postulated to be the cause of sigmoid, as opposed to normal, curvilinear, aromatic profiles. The effects of evaporative fractionation are widespread in oils throughout the United States. They are evident in approximately 75% of oils in the Gulf Coast region, and in a large proportion of the gas-condensate accumulations. The process is a major, and apparently unrecognized, means of petroleum alteration, and of generation of gas-condensates.

Experimental evidence shows that partial vaporization results in enhanced levels of light aromatic hydrocarbons in residual oils. Oil samples were partially vaporized in excess methane at elevated pressure and temperature, followed by removal of the vapour. The gas-chromatographic features of many Gulf Coast oils were reproduced. Various levels of light-end depletion and enhancement of aromaticity were brought about.

Keywords: evaporative fractionation; molecular fractionation; migration; gas-condensate; hydrocarbons (gasoline-range, aromatic, fractionation); aromatic profile; distillation; Bureau of Mines Routine Method

Introduction

The term 'evaporative fractionation' is suggested to describe a group of phenomena which appear to represent a major means of petroleum alteration. Oils which might reasonably be expected to derive from a single source, for example occurring in reservoirs in close proximity to each other in a single structure, or within the same formation in a limited geographic area, are frequently surprisingly dissimilar in their light ends. Significant variability in relative amounts of naphthenes and aromatics occurs, causing doubt as to the cogenetic nature of the oils.

A further anomaly of petroleum composition has become evident in recent years, revealed by the techniques of whole-oil capillary gas chromatography, pioneered by analysts such as F. R. Haney, H. A. Illich, T. J. Jackson, and J. Reed of Sunmark Exploration Company (Illich *et al.*, 1979). The anomaly involves 'missing' low molecular weight material, so that the chromatogram exhibits as the dominant normal-alkane n-C_{10}, n-C_{15}, or even n-C_{20}, instead of the usual form with dominant n-C_5, or n-C_6. The modified normal-alkane profile adopts a deltoid form. This phenomenon introduces uncertainty as to whether the light-end loss is natural or an artifact of production or storage.

These problems of excess aromatics and deficient light ends were partially resolved in the course of a geochemical investigation of US Gulf Coast petroleums. An unusual class of oils, distinguished by a deficiency of light ends, yet possessing abnormally high concentrations of light aromatic hydrocarbons, particularly benzene, toluene, *meta*-xylene, and *para*-xylene, and of light naphthenes (cycloalkanes), particularly methylcyclopentane, cyclohexane, and methylcyclohexane, was first encountered in reservoirs of Tertiary Age. A particularly informative instance was provided by a suite of oils reservoired adjacent to a salt dome (*Figure 1*). The oils were of diverse compositions in the gasoline range but closely similar in their heavy ends, indicating a common origin. For example, odd to even ratios in the C_{29} region average 1.05 ± 0.03, the carbon isotopic ratio of the $C_{15}+$ fractions average -27.0 ± 0.1 per ml, those of the saturated hydrocarbons average -27.4 ± 0.3, the aromatics -26.2 ± 0.2 per ml, and the pristane/phytane ratios average 1.98 ± 0.10. The oils exhibited varying degrees of light end loss quantified in *Figure 1* by the changing slope of a tie-line joining the apices of the peaks of normal-alkanes 9 and 13 in the chromatograms. The losses appeared to be

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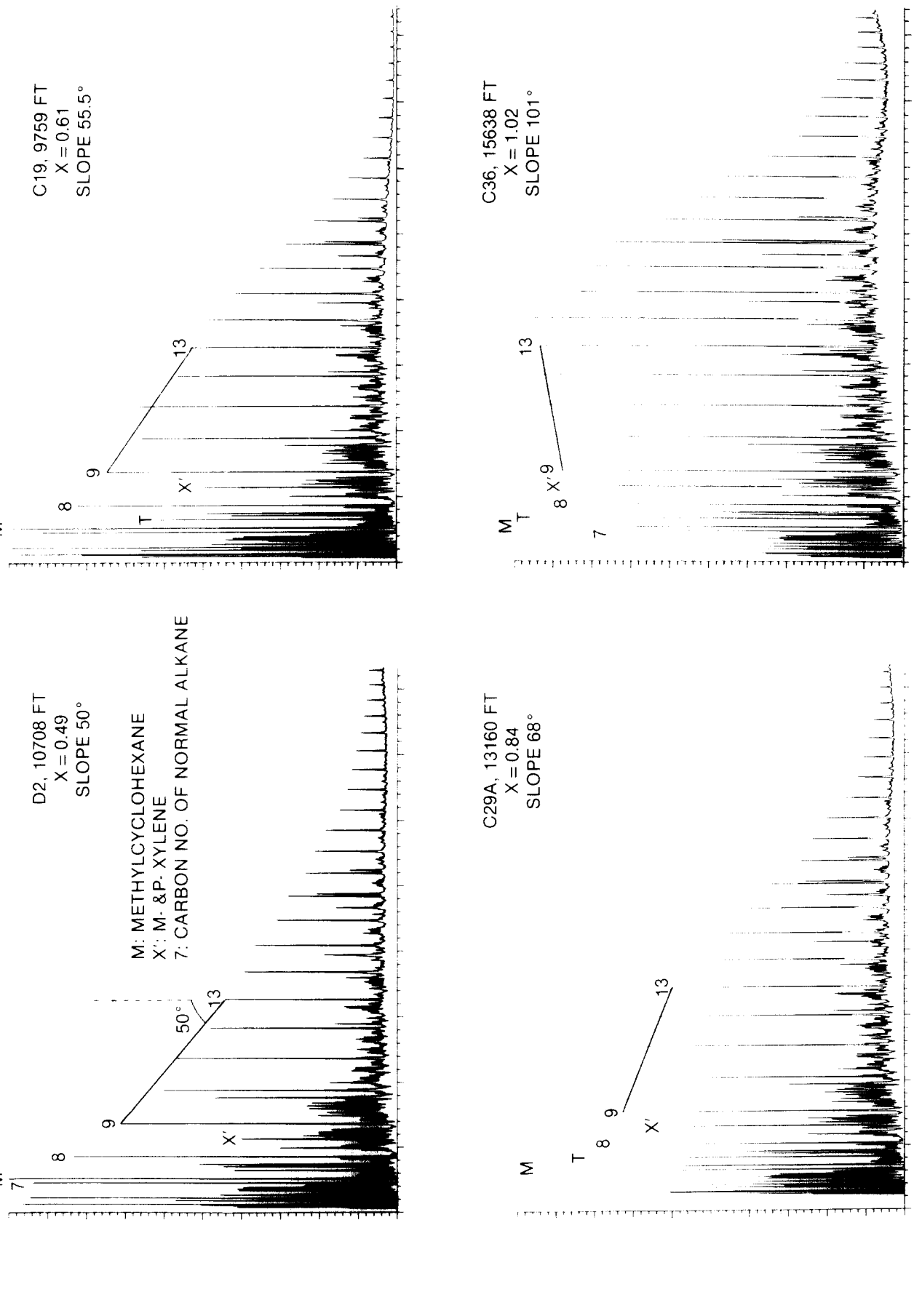

Figure 1 Genetically related oils from Tertiary reservoirs adjacent to a US Gulf Coast salt dome show progressively increasing levels of light end loss. Losses are emphasized by slope changes in the n-alkane envelope and accompanied by other compositional changes, as in the ratio xylenes/n-octane (*X*)

accompanied by fractionation, in that the oils exhibited progressive changes in certain intermolecular ratios, the extent of which was proportional to the extent of light end loss. This relationship is illustrated in *Figure 2* where increase in aromaticity (xylene/n-octane, X, and toluene/n-heptane, B) and decrease in paraffinicity (n-heptane/methylcyclohexane, F) are shown to be covariant with change in slope of the n-C_{13}–n-C_9 tie-line. Four covariant series of compositional changes were recognized: (1) increase in molecular weight of the dominant normal-alkane; (2) increase in aromaticity (in aromatic hydrocarbons relative to normal alkanes of similar molecular weight); (3) increase in 'normality' (in unbranched alkanes and cycloalkanes relative to branched isomers); and (4) decrease in paraffinicity (paraffins relative to naphthenes). This series of interrelated changes has not previously been described.

The salt dome oils suggested the possibility that the essential features of modification are the differential uptake of light hydrocarbons from oil into gaseous solution, combined with later migration of the gas, leaving residual, altered oils. Such a vaporization step, causing alteration of oil composition, is a fractionating process, whence the overall descriptive term 'evaporative fractionation'.

Experimental studies of the solubility of crude oil in gas are few. Zhuze *et al.* (1959, 1962 and 1963) determined solubility limits at various pressures and temperatures, and determined hydrocarbon group compositions in distillation fractions. They employed the data in evaluating the mode of origin of selected gas-condensate fields, concluding that several of those investigated represent oil fractions which migrated in the vapour state. Zhuze *et al.* observed and demonstrated experimentally that condensates originating in this fashion are enriched in paraffins and depleted in aromatics. These observations were repeated independently in the present investigation. Price *et al.* (1983) carried out experiments to determine the solubility of oil in gas, concluding that the process represents a viable means of primary migration of oil.

Silverman (1965) proposed the hypothesis of 'separation migration'. He postulated that the escape of existing gas-cap material along faults generates 'white' oils in daughter reservoirs by retrograde condensation, and leaves residual oils, depleted in light ends, in deeper reservoirs. His principal emphasis was a demonstration of the genetic relationship between daughter oils and residual oils. For this purpose he quoted light hydrocarbon compositional ratios. He did not employ the term 'fractionation', nor did he investigate any related concept. It is in the recognition of fractionation effects, expressed in selected intermolecular ratios, that the present work differs from, and extends, that of Silverman and Zhuze *et al.* Herein the nature of fractionation is examined theoretically and experimentally, and is quantified through the use of light hydrocarbon compositional ratios. Such ratios have not been applied in previously published solubility studies. With this information it is possible to assess the relative severity and frequency of occurrence of evaporative fractionation.

Vaporization in the reservoir

The process of vaporization visualized here involves the

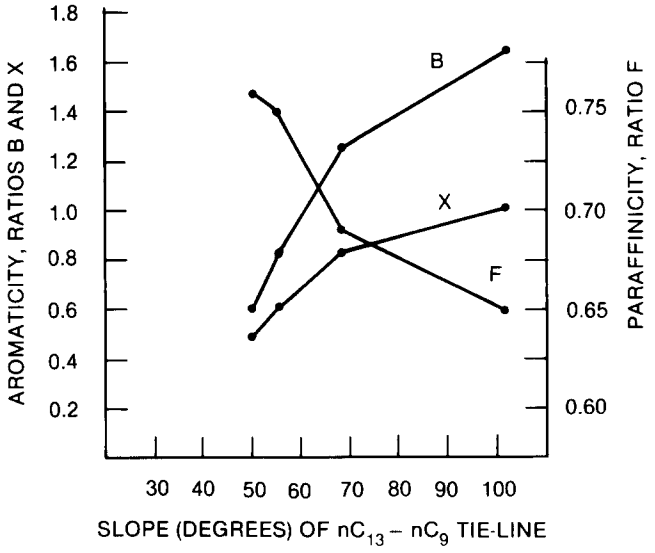

Figure 2 Compositional changes in salt dome oils are proportional to extent of loss of light ends. Ratio *B* = toluene/n-heptane; *F* = n-heptane/methylcyclohexane; *X* = (*meta*-xylene + *para*-xylene)/n-octane

intersection of an active fault with an accumulation of gas-saturated oil. The fault pathway will generate a region of reduced pressure in its vicinity. If pressure is reduced below the bubble point of the oil, exsolution of gas is immediate. Gas bubbles introduce the phenomena of two-phase flow. Oil and gas flow at substantially different rates when both are present in the pore space. Relative permeability to gas can greatly exceed that to oil. Values which are higher by a factor of approximately ten can occur, should oil saturation be reduced to 50% (Arps and Roberts, 1955). This differential is compounded with that due to differences in the viscosity of oil and gas. Typically, gas is one hundred-fold less viscous than oil under representative reservoir conditions. Using these values, the flow rate of gas would exceed that of oil by one thousand-fold. Oil is therefore substantially immobilized by progressive exsolution of gas. It is postulated that only saturated vapour migrates along the fault. The importance of this is that the separation process, of vapour from liquid, is a fractionating one. It changes not only the bulk properties of the residual oil, depleting it in light ends, but also changes certain intermolecular ratios in the remaining light ends. They are thus enhanced in aromatic and naphthenic hydrocarbons. For descriptive purposes in this study, residual oils are described as enhanced in 'aromaticity' (aromatics relative to paraffins), and diminished in 'paraffinicity' (paraffins relative to naphthenes).

The ability of a given compound to enter the vapour phase depends upon its vapour pressure, or more strictly, its fugacity. Fugacity depends upon molecular weight, isomeric structure, hydrocarbon class, and the composition of the mixture of hydrocarbons in question. The molecular weight effect is greatest among gases, for the fugacity of methane greatly exceeds that of ethane, ethane greatly exceeds propane, and propane exceeds the butanes. However, in the gasoline range there are numerous compounds of similar molecular weight. Here the effects of structure and of compound class predominate. Aromatic hydrocarbons behave anomalously compared to paraffins and naphthenes. Most aromatic compounds

possess a dipole moment which induces polarity in other molecules resulting in transitory complexes of enhanced molecular weight in the liquid phase. This limits the ability of aromatics to escape from the liquid, and therefore they accumulate in residual oils. Naphthenes are also concentrated in residual oils, but to a lesser extent. At any given carbon number iso-alkanes have a greater fugacity than n-alkanes and so are relatively enhanced in the vapour phase.

Experimental

Vaporization phenomena are customarily represented by vapour-liquid equilibrium constants, values which express the ratio of the quantities of a given compound in the vapour *versus* the liquid phase at equilibrium. Such ratios vary continuously with pressure, temperature, and the composition of the system. Considering the infinite variability of petroleum compositions, it is perhaps to be anticipated that published determinations are few, compared to the extent of potential variability. For lack of published data, experiments were carried out to establish the behaviour of key compounds. The parameters quoted below, pertaining to Experimental Series (2), are representative.

Using standard experimental equipment designed for reservoir engineering studies, a volume of 150 ml of oil was displaced into a mercury-sealed high-pressure cell. The oil was followed by 35 litres of methane, sufficient to oversaturate the oil at a final temperature and pressure of 121°C, and 6000 psi (41,370 kPa), i.e. at approximately reservoir conditions. The mixture was agitated by rocking, and equilibrated for 48 h. The cell was calculated to contain a volumetric ratio of free gas (vapour) to equilibrated oil of 0.63. In each experiment the vapour phase was bled-off under equilibrium pressure, maintained by pumping, and expanded at a valve. Liquid was condensed from the gas stream, ultimately at the temperature of solid carbon dioxide. An initial experiment and two further series of experiments were carried out. In Experiment (1) an oil of low aromaticity and high paraffinicity was employed, and was equilibrated once with high pressure methane. In Experimental Series (2) an oil of intermediate aromaticity and paraffinicity was equilibrated twice with methane. *Figure 3* shows changes in composition which took place during the most extensive experiments (Series (3)) involving eleven equilibrations. No samples of residual oil were obtained, therefore progress was monitored by analysis of the eleven condensates.

In *Figure 3*, Stages (1) and (3) represent the condensates generated in the first and third methane equilibrations or vaporization steps in Experimental Series (3). Stage (1) condensate shows the usual exponential decrease in the concentration of normal-alkanes beyond hexane (n-C_6) and resembles an unaltered, or pristine, oil. Stage (3) shows the trends which will be noticed in increasing degree in later stages: the lightest normal-alkanes are depleted, giving the overall chromatogram a deltoid profile. The principal normal-alkane is now n-C_9, nonane. Several index compounds provide generalizations concerning light hydrocarbon behaviour. Methylcyclohexane (M), is a representative cycloalkane, or naphthene, having seven carbon atoms. Its concentration is compared with

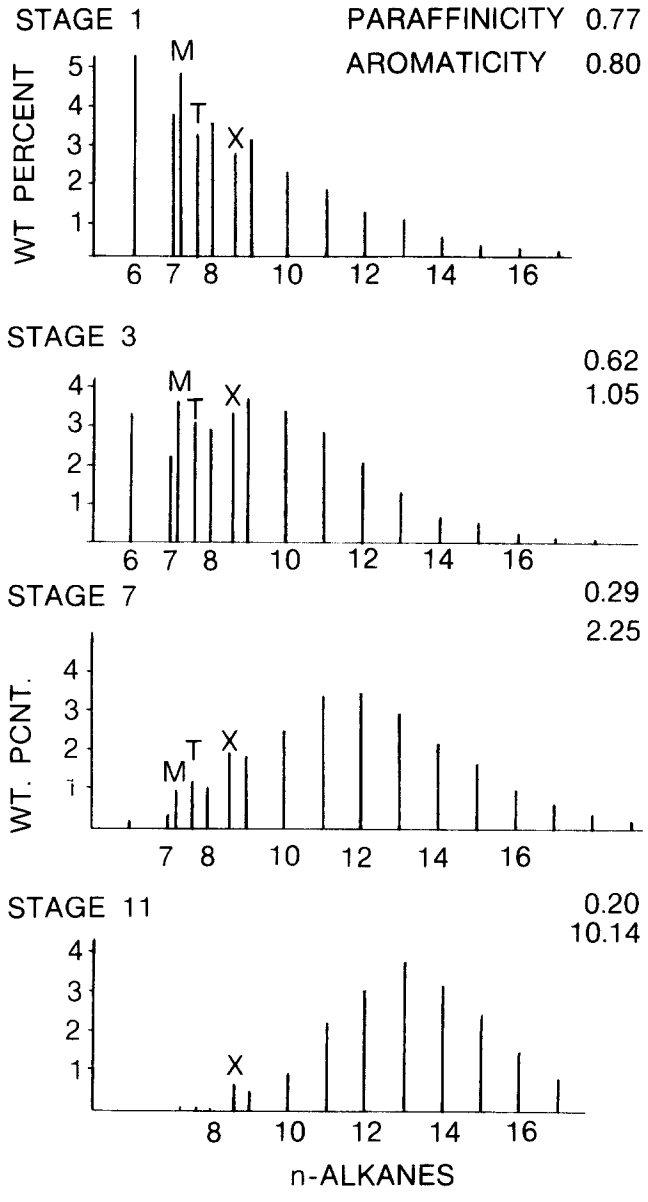

Figure 3 Products of experimental evaporative fractionation: simulated chromatograms of gas-condensates, bar heights proportional to peak areas. Light end losses result in deltoid chromatographic envelopes. Parent oils are closely similar at each stage, though more aromatic

that of n-heptane (7), a linear seven-carbon alkane, in the ratio 7/M, described as indexing 'paraffinicity'. The light aromatic hydrocarbons are represented by toluene (T), and two isomers of xylene (X), the latter forming a single chromatographic peak. The aromatics are traced by the use of the ratio X/8, representing 'aromaticity'. Vaporization results in changes in both paraffinicity, which decreases, and aromaticity, which increases. These changes are continued in Stage (7) where, due to further loss of light ends, n-C_{12} has become the dominant alkane. Methylcyclohexane, toluene, and xylene, have become the dominant compounds in the C_6 to C_9 range, paraffinicity has continued to fall, and aromaticity to increase. Stage (11) completes the series. Overall, aromaticity increased from 0.80 to 10.14, that is, 12.7-fold. Paraffinicity decreased from 0.77 to 0.20, 3.9-fold. On the basis of this comparison the process is termed 'aromatization'.

Both residual oils and condensates become progressively more aromatic and less paraffinic

simultaneously. This might be considered a contradiction to the statement that residual oils become more aromatic, and evolved gas-condensates become less aromatic at each fractionation step. Resolution simply involves consideration of the difference between the phenomena of single and multiple fractionation steps. In a series of vaporizational steps the residual oil becomes progressively enriched in aromatics, and eventually, therefore, produces aromatic condensates. Gas-condensates take on all of the significant attributes of the parent oils, including high levels of aromaticity. However, comparing any parent-daughter pair, the parent oil is more aromatic.

A summary diagram, *Figure 4*, shows the relationship of aromaticity and paraffinicity in 10 of the 14 stages of three experiments. Oils of decreasing paraffinicity and increasing aromaticity were employed as the starting materials. The data define a hyperbolic pathway. Changes along it characterize evaporative fractionation in terms of chromatographic data. Closely similar features are illustrated in the following sections by gas chromatographic data representing a group of North Slope, Alaska oils (Thompson, 1983) and a suite of gas-condensate analyses from the US Gulf Coast (Eilerts, 1957). The latter were obtained by high efficiency distillation, akin to gas chromatography.

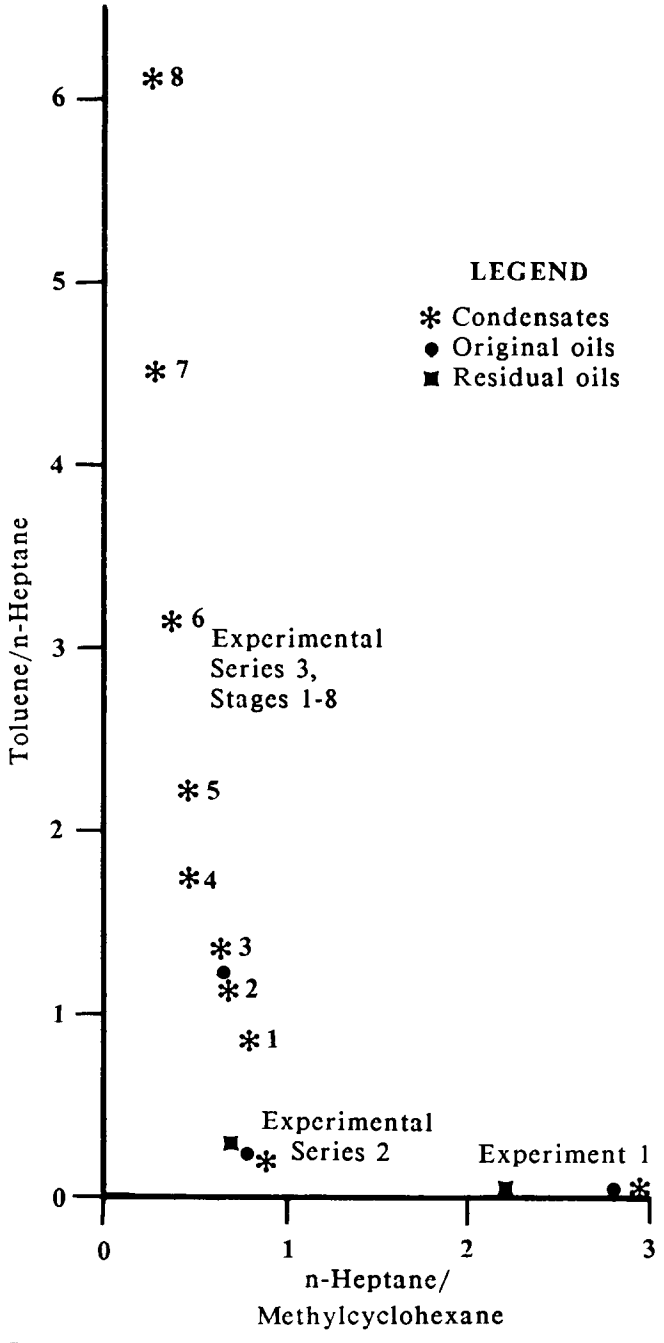

Figure 4 Toluene/n-heptane (aromaticity) *versus* n-heptane/methylcyclohexane (paraffinicity), representing the results of Experimental Series 1, 2, and 3

Recognition of evaporative fractionation in physical property data

Given the reality of evaporative fractionation and aromatization, the next significant question concerns the frequency of occurrence of the processes. There is no available suite of gas chromatographic analyses large enough to provide an answer. Alternatively, it appeared possible to evaluate the question through use of the abundant data obtained by the United States Bureau of Mines Routine Method of Oil Analysis (Smith *et al.*, 1951), if this information could be related to gas chromatographic data.

The Routine Method obtains 15 distillation fractions per sample. Each fraction is extremely broad, spreading over 8 to 15 carbon numbers. A given compound may occur in as many as 10 fractions. In the Routine Method, selected physical properties are determined for each fraction in order to empirically estimate the proportions of paraffins, naphthenes and aromatics. For the last 40 years, measurements of the specific dispersion of the lighter fractions have been reported. This property, based on differences in refractive index measured in yellow and blue light, can be empirically and uniquely correlated with the volume percent of aromatic hydrocarbons (Thorne *et al.*, 1945). Employing these measurements, aromatic profiles (Jones and Smith, 1965), depicting the broad distribution of aromatics by boiling point, can be constructed.

The key to an understanding of the Bureau of Mines data is the gas chromatographic determination of the distribution, in terms of fraction number, of the principal amounts of selected compounds. The distribution of the alkanes, methylcyclohexane, toluene, and the xylenes in terms of fraction numbers, is shown in *Figures 5* and *6*. Compound distributions were determined by gas chromatographic analysis of each Bureau of Mines distillation fraction of a representative oil.

Figure 5 represents a Mid-Continent oil of pristine nature. It exhibits a monotonic decrease in normal-alkanes accompanied by minor concentrations of naphthenes and aromatics. Such oils possess smoothly curvilinear aromatic profiles (*Figure 7*). *Figure 6* illustrates a Gulf Coast oil (Bayou Sale, Miocene, St. Mary Parish, Louisiana) inferred to have suffered extensive evaporative fractionation because it has the same chromatographic characteristics as were developed in the late stage condensates and their parental oils in Experiment (3). The substantial excess amounts of toluene in Fraction (5) and xylenes in Fraction (6) in the Bayou Sale oil result in the dramatically different appearance of its aromatic profile, *Figure 8*. The anomaly in *Figure 8* of particular significance is the decrease in specific dispersion, and in volume percent of aromatics, comparing Fractions (7)

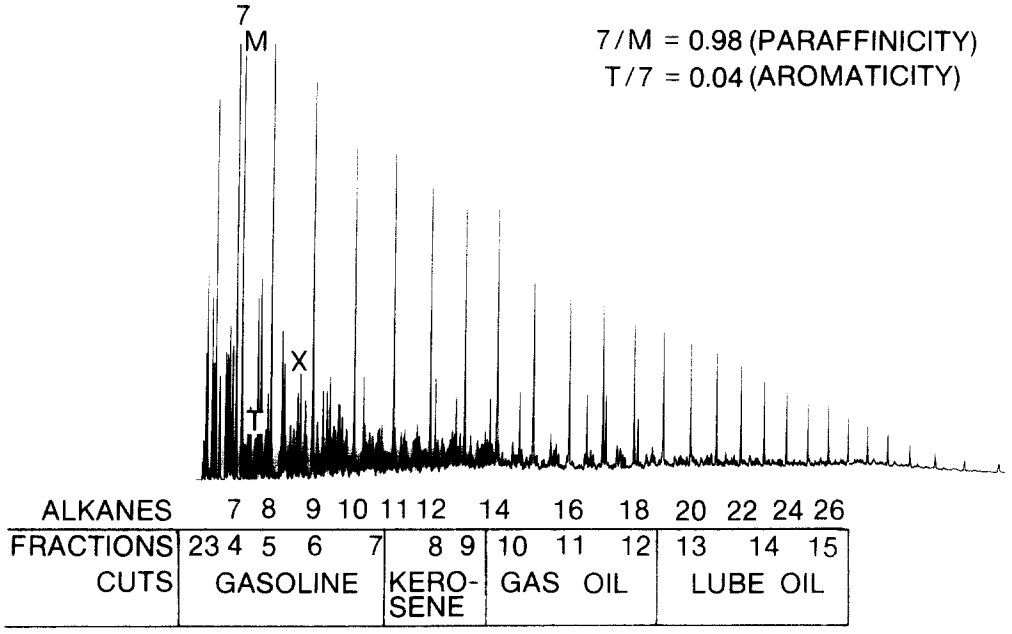

Figure 5 Relationship between gas chromatographic and distillation data representing a pristine oil, Schaben field, Kansas

and (6). The volume of aromatics in Fraction (7) normally exceeds that in (6). The reversal of trend in *Figure 6* is termed here a 'retrogression' in the aromatic profile, giving it a sigmoid form. This feature is construed below as characteristic of evaporative fractionation in distillation-physical property data. It was first reported by Jones and Smith (1965) in West Texas oils, but not explained.

Toluene, the xylenes, and in some cases benzene, play a key role in fractionation because, on one hand, they are the dominant single aromatic species in virtually all petroleums (Martin *et al.*, 1963), and on the other, because of fugacity contrasts. The dominant aromatics have substantial fugacity contrasts with respect to the paraffins and naphthenes of similar molecular weight. At higher molecular weights, in the kerosene range, as all fugacities decrease in exponential progression, the fugacity contrasts of the numerically abundant aromatic isomers present are diminished. Fractionation effects are therefore substantially less significant. They are evidently not great enough, nor is any single aromatic compound present in sufficient concentration, to cause 'superabundance' (concentration of an aromatic species greater than that of the adjacent normal-alkanes). It is suspected, however, that ethyl- and propylbenzenes, as well as naphthalenes, may also be enhanced by evaporative phenomena.

At present there is no data set comprising both gas chromatographic and distillation-physical property measurements on the same suite of oils exhibiting progressive stages of evaporative fractionation. An approach to this goal is represented, however, by two limited suites of analyses of oils from the same field. *Figure 9* represents six oils from Prudhoe Bay field, North Slope, Alaska (Thompson, 1983). The gasoline-range gas chromatographic data suggest substantial fractionation by analogy with the experimental results (*Figure 2*). Toluene exceeds n-heptane in four cases which would therefore also

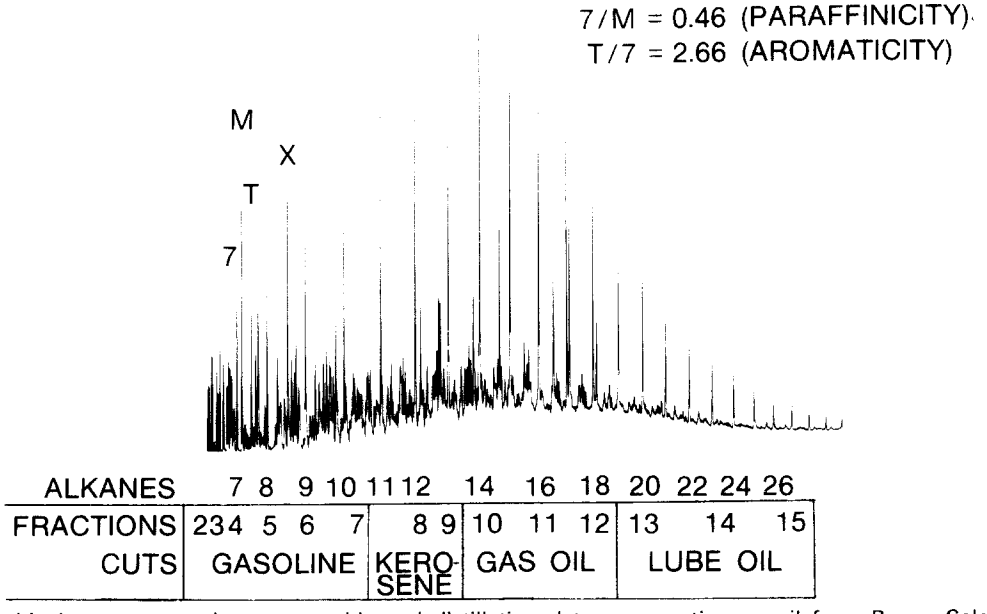

Figure 6 Relationship between gas chromatographic and distillation data representing an oil from Bayou Sale field, Louisiana, interpreted as exhibiting evaporative fractionation

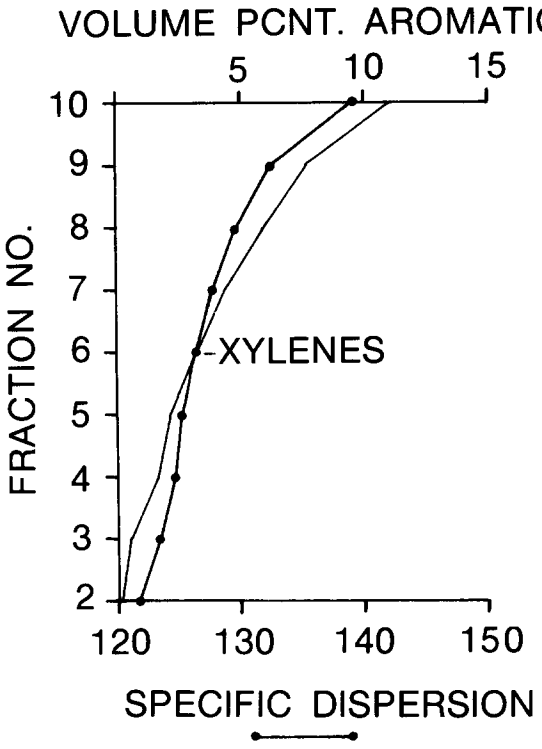

Figure 7 Normal aromatic profile based on distillation and physical property (specific dispersion) data; oil from Schaben field, Kansas

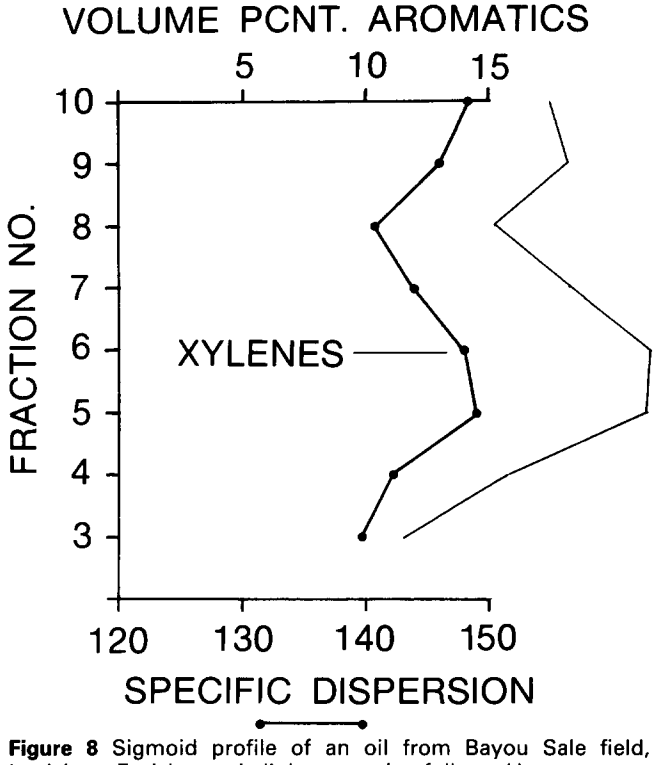

Figure 8 Sigmoid profile of an oil from Bayou Sale field, Louisiana. Enrichment in light aromatics, followed by a return to normal aromatic complements in heavier fractions, results in a curve shape which is characteristic of light end loss under reservoir conditions

exhibit superabundant amounts of xylenes. These four cases would be expected to possess sigmoid aromatic profiles. Bureau of Mines specific dispersion data for four other Prudhoe Bay oils are given in *Table 1*. Fortuitously, the available distillation analyses also show a range of conditions in the field. Case (a), *Table 1*, represents a pristine oil, having a curvilinear aromatic profile; (b) shows one retrogression in Fraction (7); (c) shows one, and appears to approach a second, while (d) shows retrogressive data in Fractions (6), (7) and (8). Even though the sample sets of *Figure 9* and *Table 1* lack common members, they concur in indicating evaporative fractionation in the fashion which is expected to be observed when a data set comprising both chromatographic and fraction-related physical property measurements becomes available. It is concluded that aromatic profiles may be employed to recognize evaporative fractionation in the absence of chromatographic data.

Frequency of occurrence of evaporative fractionation

Bureau of Mines distillation data were employed in statistical surveys of United States, and of Gulf Coast oils, to assess frequency of occurrence and degree of evaporative fractionation. Sigmoid aromatic profiles, as opposed to curvilinear forms, were construed as evidence of alteration by evaporative fractionation. The number of retrogressions in a profile was taken as an indication of the severity of alteration.

The data examined for the US comprised the profiles of volume percent aromatic hydrocarbons in Fractions (3) to (10) for 164 randomly chosen oils representing all

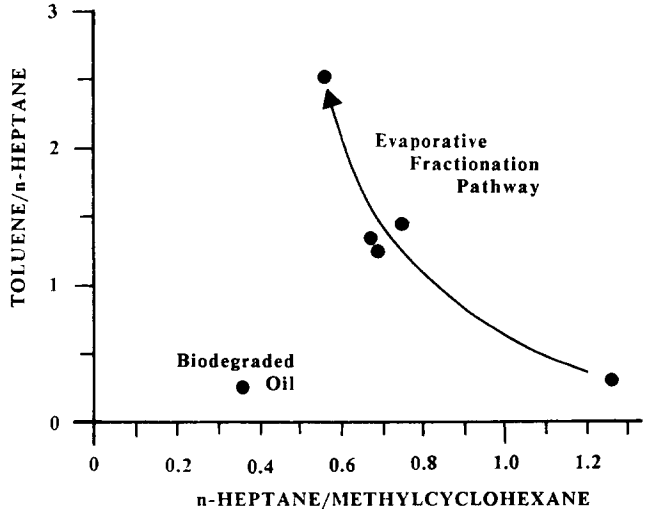

Figure 9 Toulene/n-heptane *versus* n-heptane/methylcyclohexane for oils from Prudhoe Bay field, Alaska. Properties are interpreted in terms of fractionation. Data from Thompson (1983)

Table 1 Specific dispersion data, Sadlerochit Formation oils, Prudhoe Bay Field, North Slope, Alaska, showing progressive increase in evaporative fractionation in various locations in the field

Case	Bur. Mines sample no.	Specific dispersion by fraction number								API gravity	Retrogressions
		3	4	5	6	7	8	9	10		
(a)	B71011	127.9	139.0	141.9	147.0	149.6	152.0	154.7	157.0	27.0°	0
(b)	PC-69-280	136.1	145.2	148.1	148.6	147.0	150.2	152.9	160.6	27.1°	1
(c)	PC-69-281	134.4	141.3	143.9	145.4	145.4	144.9	150.5	158.8	25.9°	1+
(d)	PC-70-283	137.4	142.2	148.9	147.9	147.4	146.2	151.9	157.3	25.7°	3

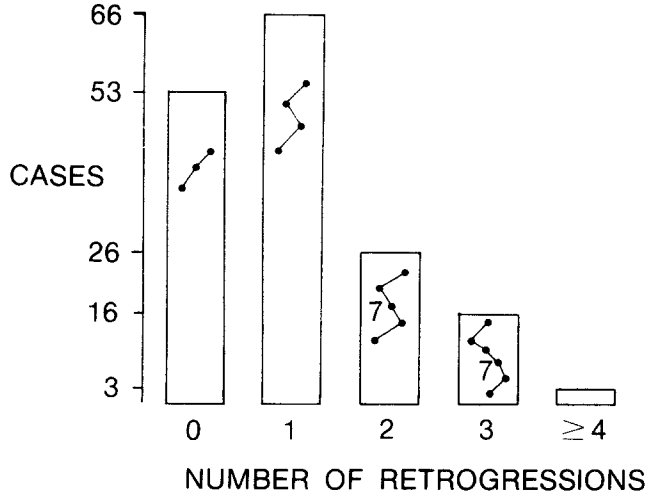

Figure 10 Frequency distribution of number of retrogressions in aromatic profiles based on specific dispersion data, 164 US oils

major producing regions except the Gulf Coast (Jurassic, Cretaceous and Tertiary reservoirs). Selection was based upon the collection of 800 analyses of major reservoirs represented in Coleman *et al.* (1978), using every third case, excluding the Gulf Coast. Aromatic hydrocarbon concentrations were obtained by way of time-share computer facilities provided as a public service by Illinois Institute of Technology, Department of Energy, Bartlesville, Oklahoma, originally the Bureau of Mines Laboratory.

Figure 10 is a histogram of the frequency of occurrence of retrogressions in aromatic profiles in US oils. The surprising result is that the majority of oils appear to exhibit some degree of fractionation. Re-examination of the 66 cases with a single retrogression showed that 17 of them were of low API gravity, apparently biodegraded, and their single retrogression occurred in Fraction 10. Such do not represent evaporative fractionation, and can conceptually be transferred to the set having zero retrogressions. Counted in this fashion, 70 cases are unaltered (42.7%), while the majority (57.3%) are slightly or strongly altered by evaporative fractionation.

A similar picture emerges in Gulf Coast Tertiary reservoirs (*Figure 11*), except that evaporative fractionation is substantially more common. The unaltered set comprises only 36 out of 158 cases, or 22.8%. The fundamental causes of the difference from the US case are unknown. In the Gulf Coast, 77.2% of the oils are altered by evaporative fractionation.

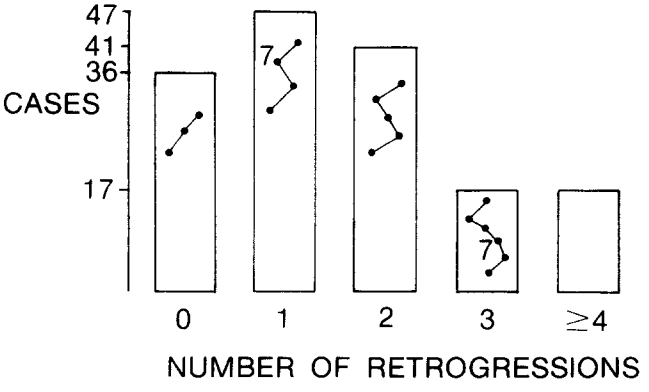

Figure 11 Frequency distribution of retrogressions in aromatic profiles representing 158 oils from US Gulf Coast Tertiary reservoirs

Insofar as fractionated oils will predictably be accompanied by accumulations of gas-condensate, it is noteworthy that the Gulf Coast is one of the most gas-prone productive regions of the United States. What factors have contributed to the occurrence of these phenomena? The nature of the deltaic sedimentary sequence, with endless repetitions of reservoir and seal lithologies, provides stacked potential traps to prevent migrant gas-condensate from escaping at the surface. The thickness of the sequence reflects the coincidental fact that one of the world's largest continental drainage systems caused sediments to prograde into a deep oceanic basin, rather than across a craton in thin sheets. Thirdly, the scale of basin and river systems was, and is, such that sediment accumulation was rapid, leading to excess pore pressures, and gravitational instability. Both features facilitate faulting and the development of fluid escape pathways. Both faulting, and the intrusion of deep-seated salt, generated structural traps. Many of these features would be expected to facilitate evaporative fractionation.

Gulf Coast gas condensates

Turning briefly to gas-condensates, once again a large data base is unavailable. However, a data set which has been accepted as representative is available. In 1957 C. K. Eilerts published his classical study entitled, '*The Phase Relations of Gas-Condensate Fluids.*' Appropriately, this was illustrated solely with reference to Gulf Coast gas-condensate accumulations. He evaluated eight reservoirs in detail and showed statistically that they were representative of the great majority in terms of composition, gas–oil ratio, and reservoir temperature and pressure. Eilerts provided sufficient data for six of the eight to facilitate the construction of *Figure 12*, based on gasoline-range

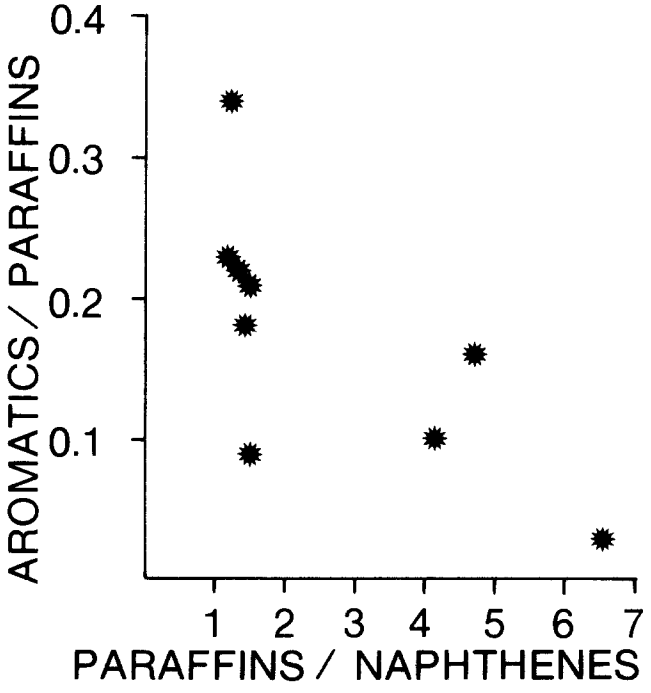

Figure 12 Ratio of aromatic/paraffinic hydrocarbons versus ratio of paraffinic/naphthenic hydrocarbons, determined by high efficiency distillation, gasoline fractions of Gulf Coast gas-condensates. Data from Eilerts (1957)

compounds. He added data on three other reservoirs for completeness. Analysis was carried out by low temperature, high-efficiency, distillation which facilitated the individual quantification of major compounds, as well as that of small groups of minor compounds. The results are closely comparable to those which would be obtained by packed-column gas chromatography in the C_4–C_8 range. Eilerts provided summary compositional data for the condensates, quoting percentages of paraffins, naphthenes and aromatics, as indicated in *Figure 12*.

The interpretation of *Figure 12* offered here is based on the premise that many Gulf Coast condensates are the products of evaporative fractionation, rather than advanced thermal cracking. The latter is commonly postulated for gas-condensates in general. *Figure 12* is not suggested to incorporate a linear correlation, rather, the data are believed to lie along a hyperbolic curve, or band, simulating the data distribution in *Figure 4*, which represents Experiments 1, 2 and 3. The initial condensates produced from pristine oils are suggested to be high in paraffin/naphthene ratios (P/N), and low in aromatics/paraffins (A/P), as are two of the data in *Figure 12*. Progressive vaporization, or vaporization at higher pressures and temperatures, would initially reduce P/N ratios, and then preferentially increase A/P ratios. Five of the data in *Figure 12* are low in P/N and simultaneously high in A/P ratios. Thus eight of the nine condensate compositions could be accounted for by progressive fractionation.

On the other hand, the distribution of data in *Figure 12* is suggested to be incompatible with a thermal cracking model for condensate generation. It is known, for example, that benzene and toluene are the most stable of all C_6 and C_7 hydrocarbons, both with reference to thermal as well as catalytic cracking (Greensfelder *et al.*, 1954). Analogously, Sawatzky *et al.* (1977) documented a 'dramatic' increase in light aromatics in a sequence of Canadian east coast oils of increasing maturity. The present author showed that P/N ratios increase steadily with catagenesis, both in extracts of sedimentary rocks (Thompson, 1979) and in mature to supermature soils (Thompson, 1983). It is therefore to be expected that if the condensates represented in *Figure 12* are highly mature, or represented a maturation trend, then high P/N ratios would be accompanied by high A/P ratios. Such is not the case, in fact the converse condition is observed. High A/P ratios are accompanied by low P/N ratios. It is suggested, in conclusion, that the properties of a representative suite of Gulf Coast condensates are more readily interpreted in terms of evaporative fractionation than in terms of thermal cracking products. The dominance of oils which exhibit fractionation and light end loss in the Gulf Coast region further argues in favour of finding the missing light material in separate reservoirs as gas-condensates.

Conclusions

Evaporative fractionation satisfactorily explains simultaneous increases in aromatics and naphthenes in the gasoline fractions of most Gulf Coast oils and condensates. Increases in aromatics are largely confined to the originally dominant and most volatile compounds (principally toluene and xylenes) generating sigmoid aromatic profiles. The majority of Gulf Coast condensates are interpreted as evaporative, rather than thermal, or source-related. Thermal condensates and supermature oils exhibit simultaneous progressive increase in both paraffinicity and aromaticity, a feature absent from Gulf Coast condensates. An evaporative origin of many onshore Gulf Coast gas-condensates is compatible with the evidence of extensive light-end loss from the majority of oils.

Severe aromatization characterizes Gulf Coast petroleums. Oils with sigmoid profiles are abundant among US oils overall, on the basis of the *prima facie* evidence of distillation data. Evaporative fractionation appears to be an extremely widespread and commonplace mode of alteration, probably as significant as bacterial degradation. Studies are now required to explicitly monitor these effects, especially in places where geological circumstances favour such processes.

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References

Arps, J. J. and Roberts, T. G. (1955) The effect of the relative permeability ratio, the oil gravity, and the solution gas-oil ratio on the primary recovery from a depletion type reservoir *Trans. Am. Inst. Min., Metall., Pet. Eng.* **204**, 120

Coleman, H. J., Shelton, Ella Mae, Nichols, Dorothy T. and Thompson, C. J. (1978) *Analyses of 800 Crude Oils from United States oil fields,* RI-78/14. Bartlesville Ener. Tech. Cent., U.S. Dept. of Energy

Eilerts, C. K. (1957) *The Phase Relations of Gas-Condensate Fluids* Am. Gas Assoc., New York, 2 vols., 962 p.

Greensfelder, B. S., Voge, H. H. and Good, G. M. (1945) Catalytic cracking of pure hydrocarbons *Ind. Eng. Chem.* **37**, 1168–1176

Illich, H. A., Haney, F. R. and Jackson, T. J. (1979) Oil geochemistry as an exploration tool *Am. Assoc. Pet. Geol. Bull.* **63**, 472

Jones, T. S. and Smith, H. M. (1965) Relationships of oil composition and stratigraphy in the Permian Basin of west Texas and New Mexico. In: *Fluids in subsurface environments, 101–224, Am. Assoc. Pet. Geol. Mem.* 4, Tulsa, OK, 414 p.

Martin, R. L., Winters, J. C. and Williams, J. A. (1963) Composition of crude oils by gas chromatography: geological significance of hydrocarbon distribution *Proc. World Pet. Cong. 6th, Frankfurt am Main 5,* p. 231–260

Price, L. C., Wenger, L. M., Ging, T. and Blount, C. W. (1983) Solubility of crude oil in methane as a function of pressure and temperature *Org. Geochem.* **4**, 201–221

Sawatzky, H., George, A. E., Banerjee, R. C., Smiley, G. T. and Montgomery, D. S. (1977) *Maturation studies of Canadian east coast oils* CANMET Rep. 77-42, Cent. Can. Technol. Miner., Dept. of Energy, Ottawa, Canada, 15 p.

Silverman, S. R. (1965) Migration and segregation of oil and gas. In: *Fluids in subsurface environments,* 53–65, Am. Assoc. Pet. Geol. *Mem.* 4, Tulsa, OK, 414 p.

Smith, N. A. C., Smith, H. M., Blade, O. C. and Garton, E. L. (1951) *The Bureau of Mines Routine Method for Analysis of Petroleum. I. The analytical method. Bull.* 490, U.S. Bur. Mines, 82 p.

Thompson, K. F. M. (1979) Light hydrocarbons in subsurface sediments *Geochem. Cosmochim. Acta* **43**, 675–672

Thompson, K. F. M. (1983) Classification and thermal history of petroleum based on light hydrocarbons *Geochim. Cosmochim. Acta* **47**, 303–316

Thorne, H. M., Murphy, W. and Ball, J. S. (1945) Determination of aromatics in light petroleum distillates by use of specific dispersions in sodium D line and mercury g line *Ind. Eng. Chem., Anal. Edn.* **17**, 481–486

Zhuze, T. P. and Yushkevich, G. N. (1959) Solubility of oil and its heavy fractions in compressed gases *Trudy Inst. Nefti Akad. Nauk SSSR* **13**, 262–274 (In Russian)

Zhuze, T. P., Ushakova, G. S. and Yushkevich, G. N. (1962) The influence of high pressures and temperatures on the content and properties of condensate in the gas phase of gas-oil deposits *Geochemistry* **8**, 797–806

Zhuze, T. P., Yushkevich, G. N., Ushakova, G. S. and Tumarev, K. K. (1963) Use of phase composition data in the system oil-gas at high pressures for ascertaining the genesis of some pools *Pet. Geol.* **7**, 186–191